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EP 0361385 A

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INT CL[5] A61L, B01D, B01J
Online: WPI AND CLAIMS

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(54) Catalyst for oxidation or decomposition of gas containing odor components

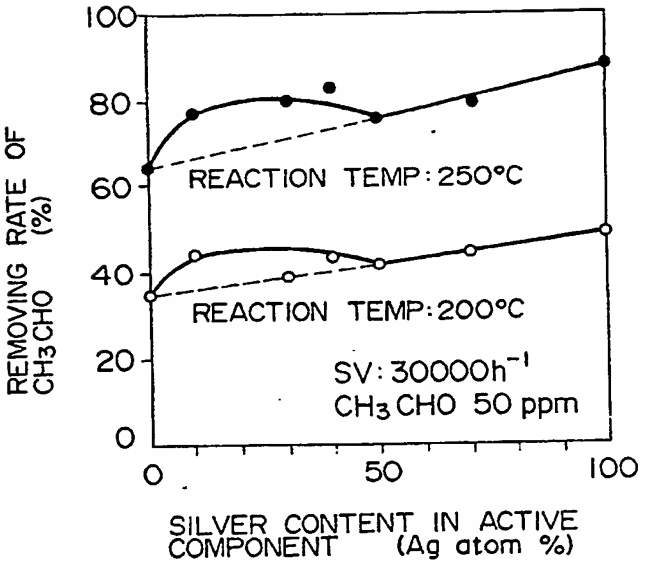
(57) A catalyst for oxidation or decomposition of a gas containing odor components at a temperature of from room temperature to 300°C in the presence of oxygen to make the gas harmless comprises a carrier and an active component supported on the carrier and contains, as the active component, silver and manganese in an atomic ratio of silver to manganese of 5:95 to 50:50.

The silver and manganese are in the form of their oxides or a silver, manganese and oxide complex.

Specific compounds destroyed by the catalyst in examples are acetaldehyde, methyl mercaptan and trimethylamine.

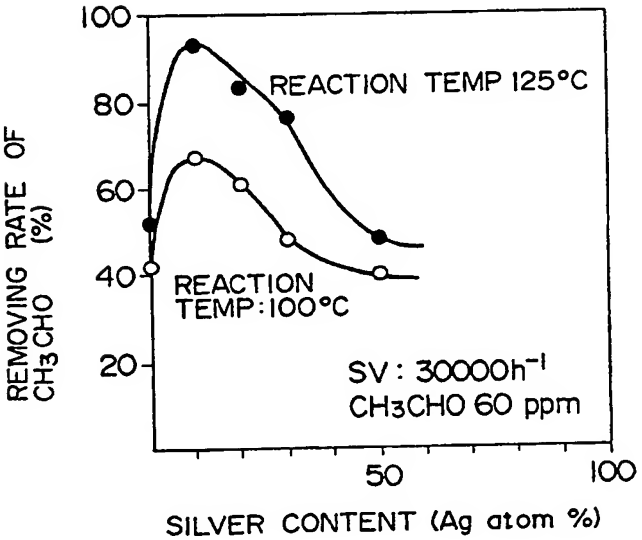
GB 2 238 486 A

FIG. 1



SILVER CONTENT AND CH_3CHO REMOVING ACTIVITY OF Ag/Mn CATALYST SUPPORTED ON $\gamma-Al_2O_3$

FIG. 2



DEPENDENCE OF ACTIVITY OF Ag/Mn BULK CATALYST ON SILVER CONTENT

FIG. 3
(COMP. EX. 1)

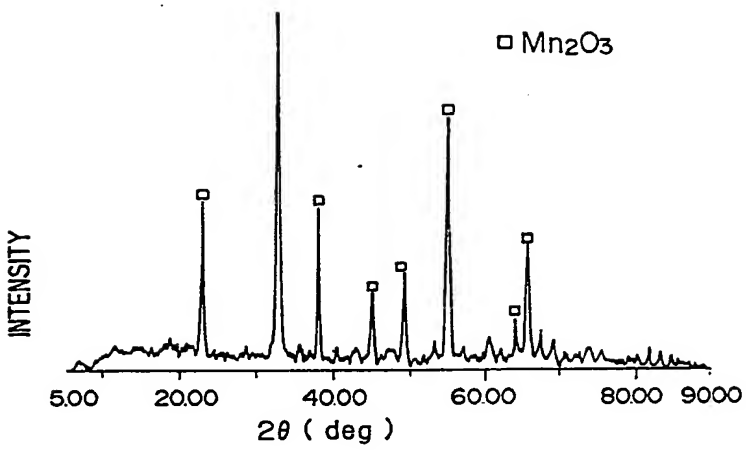
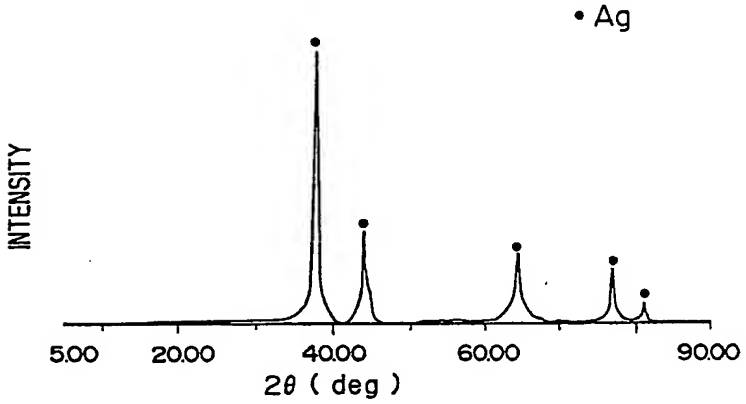


FIG. 4
(COMP. EX. 2)



Ag/Mn = 2/1 500°C

FIG. 5
(COMP. EX. 3)

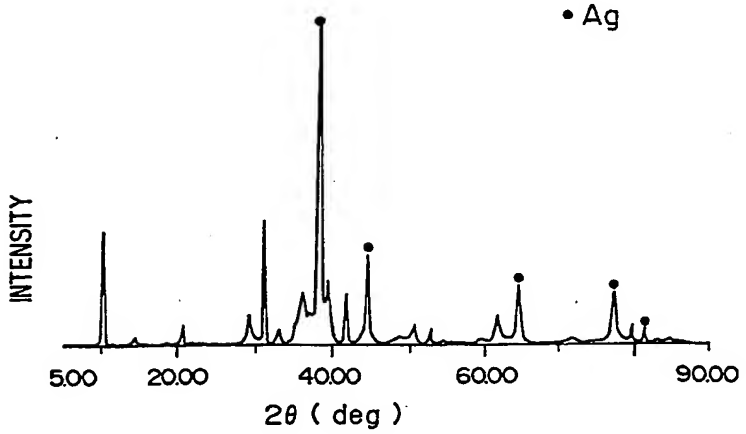


FIG. 6
(EX. 2)

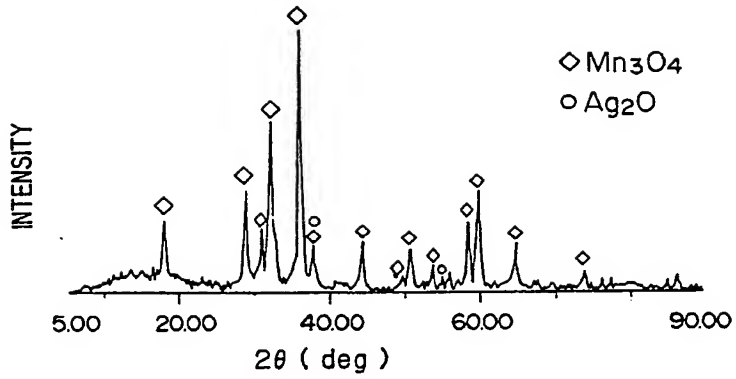


FIG. 7
(EX. 4)

Ag/Mn=3/7 500°C

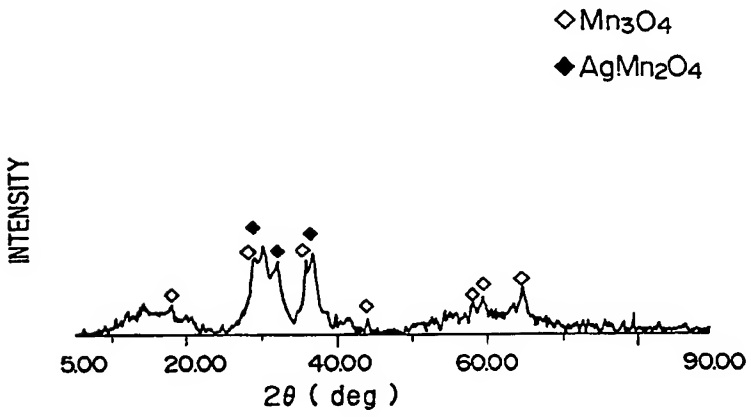


FIG. 8

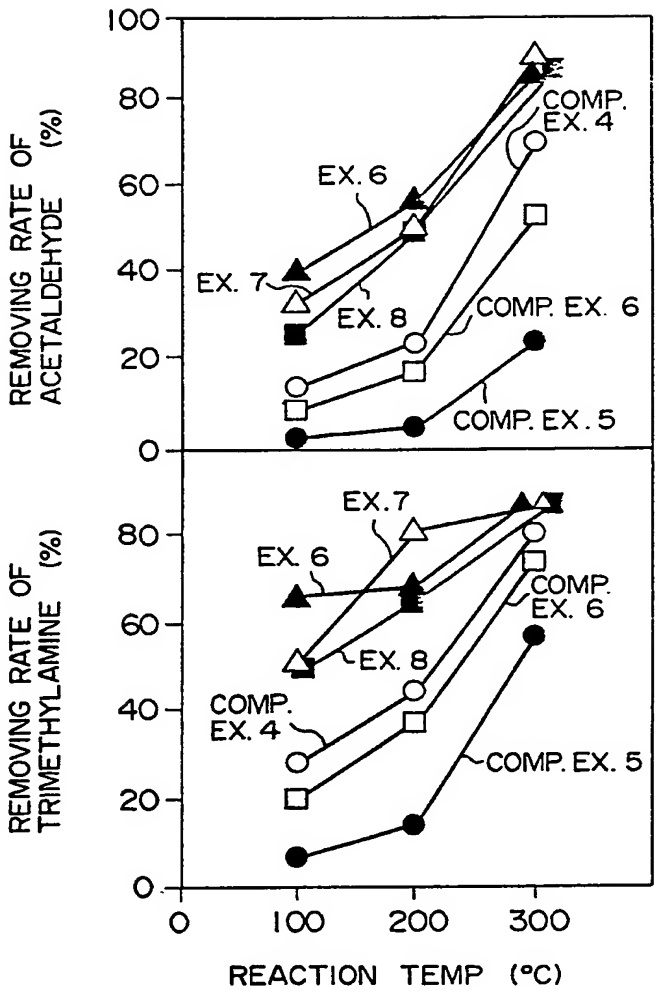

REMOVING RATE OF ACETALDEHYDE (%)
100
80
60
40
20
0
EX. 6
EX. 7
EX. 8
COMP. EX. 4
COMP. EX. 6
COMP. EX. 5
REMOVING RATE OF TRIMETHYLAMINE (%)
EX. 7
EX. 6
EX. 8
COMP. EX. 4
COMP. EX. 6
COMP. EX. 5
0
100
200
300
REACTION TEMP (°C)

FIG. 9

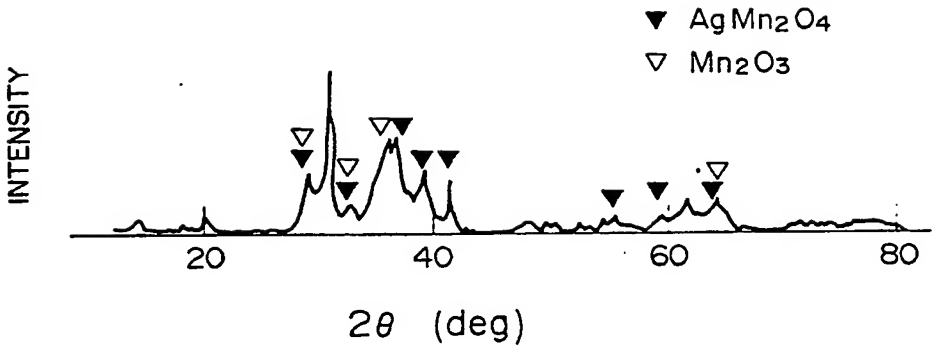


FIG. 10

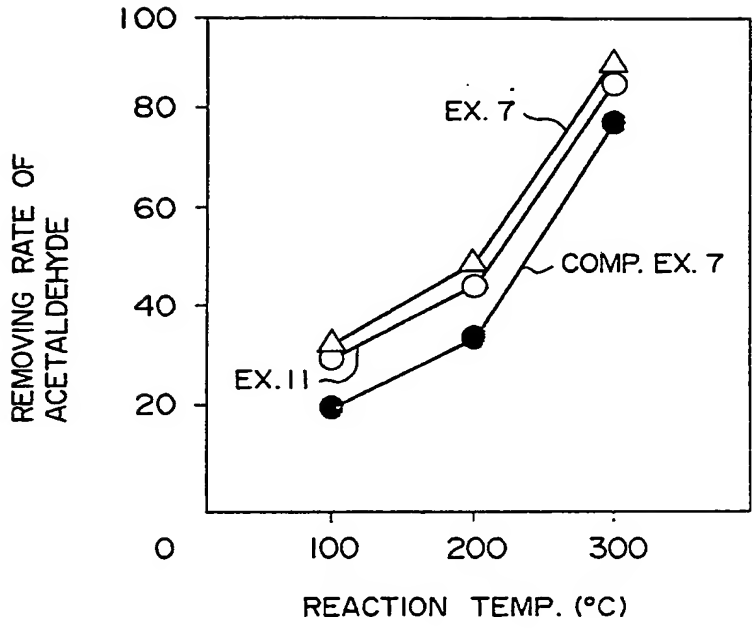

100
80
60
40
20
0
100
200
300
REMOVING RATE OF ACETALDEHYDE
REACTION TEMP. (°C)
EX. 7
COMP. EX. 7
EX. 11

FIG. 11

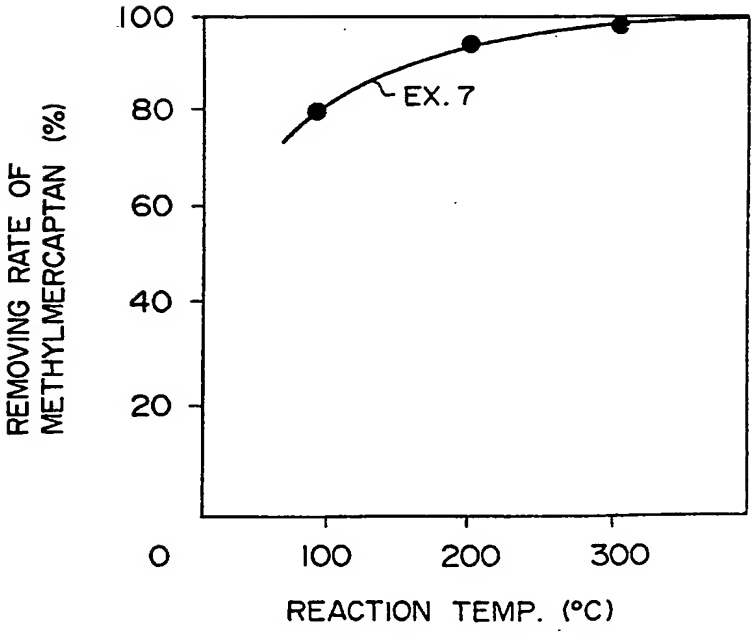

100
80
60
40
20
0
100
200
300
REMOVING RATE OF METHYLMERCAPTAN (%)
REACTION TEMP. (°C)
EX. 7

FIG. 12

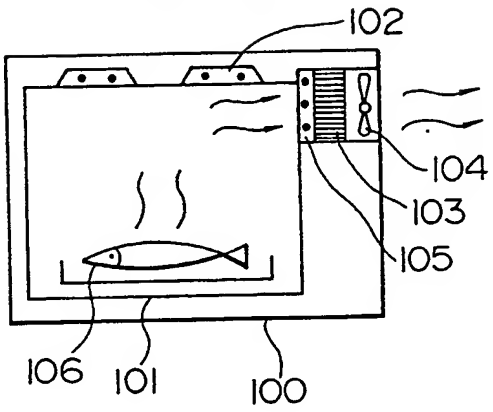


FIG. 13-1

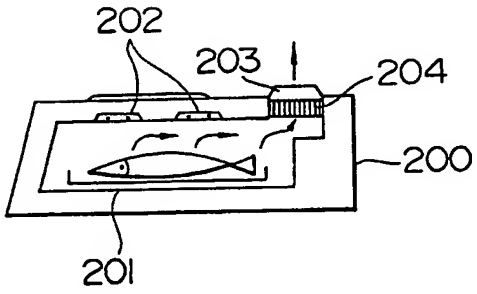


FIG. 13-2

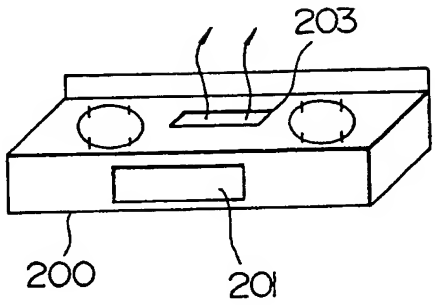
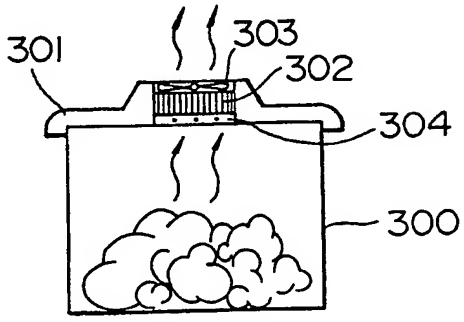


FIG. 14



CATALYST FOR OXIDATION OR DECOMPOSITION OF GAS CONTAINING ODOR COMPONENTS

The present invention relates to an oxidation or decomposition catalyst containing a novel active component and in particular to a catalyst for oxidation or decomposition of industrial off-gases and gases containing odor components harmful and unpleasant to human beings and natural environments which are generated from household appliances and housing facilities at a low temperature region between room temperature and 300°C.

For these last ten years there have been continuously raised objections and problems on life environments such as traffic noises and atmospheric pollution and pollution of rivers caused by gases harmful to human bodies and disagreeable odor gases which are exhausted from factories. Techniques of catalytic combustion of industrial gases or gases discharged from automobiles on catalysts to make them harmless have been employed from the 1970's and noble metals such as Pt, Pd, and Rh have been generally used as active components of the catalyst. Such catalytic combustion method is further applied to various combustors and heaters as

clean combustion method generating no NOx and noble metals are also generally used as active components of the catalyst. However, noble metal catalysts are expensive. Oxide catalysts which are inexpensive and high in performance have been desired. For answering such a demand, there have been proposed binary oxide catalysts comprising silver oxide and manganese oxide for catalytic combustion of hydrogen (Japanese Patent Kokai No. 55-88850) and ternary oxide catalysts comprising oxides of silver, cobalt and manganese for catalytic combustion of carbon monoxide and hydrocarbons (Japanese Patent Kokai No. 55-88855).

Recently, especially, need for removal of gases harmful to human body and disagreeable odor gases which are generated in room increases with more strict regulation on exhaust gases and with changing life style calling for more comfortable life circumstances. Sources of hamful gases and disagreeable odor gases in room include household combustors such as heaters, cooking utensils, kitchen utensils, raw garbages, lavatory, etc. Gases discharged from such household devices contain not only carbon monoxide and hydrocarbons which are uncombusted fuel components, but also various odor and harmful components such as aldehydes, amines, alcohols, and mercaptans. These gases are at low temperatures from room temperature to about 300°C. Therefore, desirable catalysts for disposal of off-gases have been those which have a high activity at a low temperature and are

low in production cost. However, the above-mentioned known catalysts are directed to catalytic combustion of hydrogen, carbon monoxide and hydrocarbons and are insufficient for treatments of off-gases containing many of the above odor components other than hydrogen, carbon monoxide and hydrocarbons.

An object of the present invention is to provide a catalyst for oxidation or decomposition of odor gases, especially off-gases containing various kinds of harmful and odor components which are generated in rooms.

Another object of the present invention is to provide a catalyst for oxidation or decomposition which exhibits a high activity at a low temperature of room temperature to 300°C in oxidation and decomposition of off-gases containing odor components which are generated in households.

The oxidation or decomposition catalyst of the present invention is a catalyst for oxidizing or decomposing a gas containing odor components in the presence of oxygen to make it harmless, which is characterized in that it comprises a carrier and an active component supported on the carrier; the active component contains silver and manganese in an atomic ratio of silver to manganese

of 5:95 to 50:50; the silver is present in the form of at least one of a compound with oxygen and a compound with oxygen and manganese; manganese is present in the form of at least one of a compound with oxygen and compound with oxygen and silver; and the manganese oxide contains manganese atoms having an oxidation number of less than +4.

Suitable carriers for the oxidation or decomposition catalyst are porous carriers having a specific surface area of 0.5 m^2/g or more such as γ-alumina, TiO_2, zeolite, silica and cordierite, because the supported active components agglomerates if the specific surface area of the carrier is smaller. Upper limit of the specific surface area is preferably 1000 m^2/g. Especially a suitable range is 50-1000 m^2/g.

The above catalyst may also be used as a catalyst body comprising a substrate of ceramics or metal and the catalyst coated thereon. The substrate may be a honeycomb substrate, a plate-like substrate and a metal gauze.

The present invention will be explained in detail below.

The catalyst of the present invention is obtained by adding an aqueous solution of a neutralizing agent such as ammonia, an alkali carbonate, or an alkali hydroxide to a mixed aqueous solution of silver nitrate and water-soluble manganese salts such as manganese nitrate, drying the resulting coprecipitate and then

oxidizing it with heating or separately producing precipitates of silver and manganese by the above process, kneading them, drying the mixture and then oxidizing the mixture with heating. The catalyst can also be produced by wet or dry mixing or kneading of a silver salt such as silver oxalate, silver carbonate or silver nitrate or silver oxide with a manganese salt such as manganese acetate, manganese oxalate or manganese nitrate or manganese oxide and then heat decomposing the mixture.

The resulting catalyst is finally subjected to heat treatment at 200-900°C, preferably 300-600°C in the presence of an oxygen-containing gas.

The catalyst of the present invention can contain, as an active component, at least one of iron, cobalt, nickel, copper, vanadium, and zinc, and noble metals of Group VIII of the periodic table such as platinum and palladium in addition to silver and manganese elements. Content of the elements other than silver and manganese is preferably 1-10% by atom. For example, if cobalt is contained in an amount of more than 10% by atom, $AgCoO_2$ is produced in a crystallized state to reduce the activity of catalyst. If it is contained in an amount of less than 1% by atom, effect of addition is insufficient.

Mainly, Co is present in the form of CoO or Co_3O_4, Fe is present in the form of Fe_2O_3, Ni is present in the form of NiO, Cu is present in the form of CuO or

Cu_2O, V is present in the form of V_2O_5, Zn is present in the form of ZnO, Pd is present in the form of PdO or Pd, and Pt is present in the form of Pt.

Silver element of the thus produced Ag/Mn binary catalyst forms a compound with oxygen or with oxygen and manganese element. That is, silver is not precipitated in a metallic form, but is in an oxidation state in the sense of an electron state. Usually, in the case of silver single component catalyst, Ag_2O releases oxygen at higher than about 350°C and is precipitated as Ag at 300-600°C which is a preferable heat treating temperature for the present invention. However, in the catalyst of the present invention, manganese oxide is present in the state of oxide of manganese atom lower in oxidation number than the normally stable oxidation number of manganese atom in MnO_2, namely, in the state of lower than +4 in oxidation number of manganese atom, thereby to keep silver in an oxidization state. As a result, the catalyst becomes highly active to the oxidation reaction and, besides, silver is highly dispersed in the catalyst and agglomeration of particles can be suppressed.

Forms of compounds of silver and manganese elements of the catalyst can be identified by powder X-ray diffraction (XRD), and the electron state (oxidization number) can be identified by an ordinary method such as X-ray photoelectron spectroscopy (XPS).

The catalyst of the present invention which

is mainly composed of silver and manganese can be used as it is, but preferably supported on porous carriers such as alumina, titania, and zeolite; ceramics carriers such as cordierite; and metallic carriers such as stainless steel, whereby the catalyst activity can be sufficiently obtained. Furthermore, the catalyst supported on the above carrier can further be supported on a substrate such as ceramics or a metal by coating, etc.

These catalysts can be prepared, for example, by the following process: The precipitate containing silver and manganese which is obtained by the aforementioned process or oxides obtained by heat treatment thereof or salts of silver and manganese are mixed and kneaded with a carrier such as alumina or titania, or a precursor sol thereof and then the mixture is heat treated or the mixture is coated on a ceramic carrier such as alumina or titania or a metallic carrier and then, heat treated. Alternatively, a mixed aqueous solution of a water-soluble silver salt and manganese salt is impregnated in or coated on a ceramic carrier or a metallic carrier and then dried and heat treated to preciptate a catalyst mainly composed of silver and manganese.

The shape of catalyst prepared by the above process may be pellets molded from the powders, honeycomb, sheet, plate, three-dimensional foam, etc.

The catalyst of the present invention comprises

mainly silver and manganese and contains silver in the form of a silver oxide and/or an oxide of silver and manganese, and manganese in the form of a manganese oxide and/or an oxide of manganese and silver, and furthermore the manganese oxide contains a manganese atom of oxidation number of less than +4. The manganese oxide is present mainly in the form of Mn_2O_3 and/or Mn_3O_4. Part of silver in the catalyst forms a double oxide with manganese. The form of the double oxide depends on heat treating temperature and includes forms of $AgMn_2O_4$, $AgMnO_2$, $AgMnO_4$, AgMnO, Ag_2MnO_2, or $Ag_2Mn_8O_{16}$ or a mixture thereof. The double oxide is most preferably in the form of $AgMn_2O_4$ or $AgMnO_2$.

The catalyst shows high activity for the following reasons: That is, the oxidation state of silver can be maintained by forming a double oxide of silver and manganese; silver is highly dispersed to suppress its agglomeration; and the double oxide is mixed with manganese oxide resulting in high dispersion of silver. The oxidation state of silver is maintained by keeping the manganese atom of manganese oxide in an oxidation state of less than +4 in oxidation number. The growth of crystal of double oxide of silver and manganese is also suppressed by mixing the double oxide with manganese oxide.

All of the silver in the catalyst may not be in the form of compound, but part of silver may be present in the form of silver (metallic state) because silver is

mixed with manganese oxide and thus it is thermally stable and highly active than in a single state.

The catalyst of the present invention is especially effective for deodorizing harmful and disagreeable odor gases of low concentration containing various components which are generated by cooking foods in an oven, grill or electronic oven.

When the catalyst of the present invention is employed for these purposes, it is preferred to provide it at the place inside the oven, grill or electronic oven where the gas containing odor components generated by cooking is dominant, that is, the place giving no obstacles to the cooking, for example, the gas exhaust passage, the inlet or outlet of the gas.

The catalyst of the present invention effectively works at room temperature or higher, preferably 100-300°C. Temperature of disagreeable odor gases may be at a lower temperature, depending upon cooking conditions. In such case, it is desirable to keep the catalyst in the temperature range which the catalyst works effectively by providing a heater or the like to make the catalyst work effectively.

The catalyst of the present invention can be applied to cooking utensils such as an oven, a gas oven, electronic oven and a gas table; apparatuses for disposal of industrial wastes such as refuse incinerator and wet refuse deodorizer, vehicles for carrying men or cargoes, such as automobiles, electric tram cars, and airplanes;

toilet; and exhaust gas purification apparatuses for automobiles.

When the catalyst is applied to the oven, gas oven or electronic oven, the present catalyst is preferably provided in the form of a layer in passages for discharging a gas from the grill. The gas in the grill is discharged through the catalyst layer by natural convention or by suction with an exhaust fan. The catalyst layer is desirably kept at a temperature within a range of room temperature to 300°C. For heating the catalyst layer, it is preferred to provide a heater for heating the catalyst layer at a position before the catalyst layer in the passage for discharging the gas from the grill.

When the catalyst is applied to a gas table, it is desired to provide a catalyst layer at a position before an exhaust vent for discharging smoke. The catalyst layer is preferably kept at a temperature within a range of room temperature to 300°C. This temperature range is kept preferably by adjusting the distance from the grill heater to the catalyst layer.

When the catalyst is applied to apparatuses for disposal of industrial wastes such as refuse incinerator, the catalyst layer is preferably provided at the position in the passage up to a chimney for the smoke generated in the refuse incinerator and containing odor components. The catalyst layer is kept at a temperature within a range of room temperature to 300°C.

When the catalyst is applied to a wet refuse

deodorizer, an exhaust vent for discharging the gas generated from wet refuse and containing odor components is provided at a deodorizing container and the catalyst is preferably provided in the form of a layer in the exhaust vent. It is desired to provide a heater for heating the catalyst layer in the exhaust vent to keep the catalyst temperature within a range of room temperature to 300°C. It is also desired to provide a fan at a position after the catalyst layer in the exhaust vent.

When the catalyst is applied to vehicles for carrying men or cargos such as automobiles, electric tram cars and airplanes, the catalyst is preferably provided in the form of a layer near the position where the gas containing odor components are generated in the vehicles. For example, it is desired to provide a container having the catalyst layer and a fan which sucks the gas containing odor components near the position where men or cargoes are present.

When the catalyst is applied to toilets, the catalyst is preferably provided in the form of a layer in an exhaust vent for toilets. In order to keep the catalyst layer at a temperature of room temperature to 300°C, it is preferred to provide a heater for heating the catalyst layer.

The catalyst layer is desirably of cartridge type in order that it can be replaced with a new one

when its activity in deteriorated. Specifically, a carrier on which catalyst active components are supported is provided on a honeycomb-like or mesh-like substrate by coating or other means and when it becomes necessary to exchange the catalyst layer, the cartride containing the catalyst layer can be exchanged as it is. The substrate can be made of a metal or ceramics such as cordierite.

The present catalyst can be used by contacting a gas containing odor components with the catalyst in the presence of oxygen at a temperature of room temperature to 300°C.

The present invention will now be described in greater detail by way of examples with reference to the accompanying drawings, wherein:-

Fig. 1 is a graph which shows relations between the acetaldehyde removing rate and the content of silver in active components when acetaldehyde was subjected to a catalytic combustion using the catalyst prepared in Example 1 and the catalyst prepared in Comparative Example 1.

Fig. 2 is a graph which shows relations between the acetaldehyde removing rate and the content of silver in active components when acetaldehyde was subjected to a catalytic combustion using the catalysts prepared in Examples. 3, 4, and 5 and Comparative Example 1.

Figs. 3-7 show X-ray diffraction patterns of the catalysts prepared in the examples of the present invention and comparative examples.

Fig. 8 is a graph which shows acetaldehyde removing rate and trimethylamine removing rates at various temperatures using the catalysts prepared in Examples 6, 7, and 8 and Comparative Examples 4, 5 and 6.

Fig. 9 shows an X-ray diffraction pattern of the catalyst prepared in Example 9.

Fig. 10 is a graph which shows relations between the acetaldehyde removing rate and the reaction temperature when acetaldehyde was subjected to a catalytic combustion using the catalysts prepared in Examples 7 and 11 and Comparative Example 7.

Fig. 11 is a graph which shows relations between the methylmercaptan removing rate and the reaction temperature when methylmercaptan was subjected to a catalytic combustion using the catalyst prepared in Example 7.

Fig. 12 is a rough sketch of an oven provided with the catalyst of the present invention.

Fig. 13-1 is a rough sketch of the side view of a gas table provided with the catalyst of the present invention.

Fig. 13-2 is a rough sketch of oblique view of the gas table of Fig. 13-1.

Fig. 14 is a rough sketch of a wet refuse deodorizer provided with the catalyst of the present invention.

Preferred Embodiments of the Invention

The following nonlimiting examples will further explain the present invention in detail.

Example 1

2.276 g of silver nitrate and 40.436 g of manganese nitrate hexahydrate were dissolved in distilled water to make 300 cc of a solution. This mixed aqueous solution was uniformly absorbed in 500 g of γ-alumina powder (2-4 mm in diameter in spherical shape). Then, the powder was dried at 120°C and heat treated at 500°C for 2 hours in air atmosphere to prepare an Ag/Mn catalyst supported on γ-alumina. Compositional ratio of Ag/Mn in the active components was Ag:Mn=10:90 (content of silver: 10% by atom) and the amount of active components supported was 2 wt% based on the carrier after the heat treatment at 500°C. In the same manner, Ag/Mn catalysts supported on γ-alumina having ratios Ag/Mn (atomic ratio) of Ag:Mn=20:80, 30:70, 40:60, 50:50, and 70:30 were prepared. Furthermore, a catalyst of 100% Mn and 100% Ag supported on γ-alumina was also prepared in the same manner as above. Fig. 1 shows relations between reaction rate of odor component acetaldehyde and content of silver in the catalyst at reaction temperatures 200°C and 250°C. In the range of 50% by atom or less in content of silver, effect of silver and manganese as a double oxide was exhibited and addition of silver in a small amount resulted in an increase of activity of a manganese

single component catalyst.

Example 2

8.4935 g of silver nitrate and 129.168 g of manganese nitrate hexahydrate were dissolved in distilled water to make 1500 cc of a solution. To this mixed aqueous solution was added dropwise aqueous ammonia obtained by diluting concentrated aqueous ammonia with distilled water twice in volume with stirring until pH reached 9. The produced precipitate was washed by decantation, then subjected to suction filtration and dried at 120°C. This was fired at 500°C for 2 hours. The powder was press molded and classified into 10-20 meshes to obtain an Ag/Mn catalyst. This catalyst had an atomic ratio of Ag:Mn=10:90.

Example 3

Example 2 was repeated except that 16.987 g of silver nitrate and 114.816 g of manganese nitrate hexahydrate were used, thereby to obtain an Ag/Mn catalyst having a compositional ratio (atomic ratio) of Ag:Mn=20:80.

Example 4

Example 2 was repeated except that 25.4805 g of silver nitrate and 100.464 g of manganese nitrate hexahydrate were used, thereby to obtain an Ag/Mn catalyst having an atomic ratio of Ag:Mg=30:70.

Example 5

Example 2 was repeated except that 33.974 g of silver nitrate and 114.816 g of manganese nitrate hexahydrate were used, thereby to obtain an Ag/Mn catalyst having an atomic ratio of Ag:Mn=50:50.

Comparative Example 1

Example 2 was repeated except that silver nitrate was not used and 143.52 g of manganese nitrate hexahydrate was used, thereby to obtain a manganese oxide single component catalyst.

Comparative Example 2

85 g of silver nitrate was fired at 500°C for 2 hours and the resulting powder was ground and then press molded and classified into 10-20 mesh to obtain an Ag single component catalyst.

The catalyst of the above Examples 1-5 is provided, for example, in the exhaust vent of an oven, a gas oven, an electronic oven or the like and is used as a deodorizing catalyst for a gas containing odor components. An example where the catalyst of the present invention is provided in an oven is shown in Fig. 12 and an example where the catalyst of the present invention is provided in a gas table is shown in Figs. 13-1 and 13-2. In Fig. 12, reference numeral 100 indicates an oven body, 101 indicates a grill, and 102 indicates a heater for the grill. The numeral 103 indicates a

catalyst provided in an exhaust vent, 104 indicates an exhaust fan, and 105 indicates a heater for heating the catalyst. The numeral 106 indicates food to be cooked, which is a fish here. Structurally, the same can be applied to the cases where the catalyst is applied to a gas oven and an electronic oven.

In Fig. 13-1 and Fig. 13-2, 200 indicates a gas table body, 201 indicates a grill for grilling food such as a fish, 202 indicates a heater for grill, 203 indicates an exhaust vent for a gas containing odor components generated by heating the food to be cooked, and 204 indicates a catalyst layer provided in the exhaust vent.

In these cooking utensils, acetaldehyde is generated as an odor component in cooking.

Reaction rate of odor component acetaldehyde was measured when the catalysts prepared in Examples 3, 4 and 5 and Comparative Example 1 were used. Fig. 2 shows relations between the reaction rate at reaction temperatures of 100°C and 125°C and the content of silver. As in Fig. 1, use of the catalysts of Examples 3, 4 and 5 resulted in much increase of activity at a silver content of 50% by atom or less as compared with use of the manganese single component catalyst of Comparative Example 1 and showed maximum activity at a sivler content of 10% by atom.

Comparative Example 3

Example 2 was repeated except that 67.948 g

of silver nitrate and 57.408 g of manganese nitrate hexahydrate were used, thereby to obtain an Ag/Mn catalyst having an atomic ratio Ag:Mn=67.33.

Figs. 3-7 show powder X-ray diffraction patterns of the catalysts prepared in Comparative Examples 1, 2 and 3 and Examples 2 and 4. Fig. 3, Fig. 4, Fig. 5, Fig. 6 and Fig. 7 show diffraction pattern of the catalysts of Comparative Example 1, Comparative Example 2, Comparative Example 3, Example 2 and Example 4, respectively. The manganese single component catalyst of Comparative Example 1 is in the form of crystal of Mn_2O_3 and the silver single component catalyst of Comparative Example 2 is in the form of crystal of Ag (metallic state). On the other hand, peak of Mn_3O_4 and peak of a part of Ag_2O were recognized in XRD pattern of Example 2. The Ag/Mn catalyst had a crystal form different from that of single component catalyst due to its double oxide effect. In order to know more detailed state of oxidation number, bound energy of silver atom and manganese atom was measured by X-ray photoelectron spectroscopy. The manganese atom in the catalyst of Exampel 2 was in a somewhat lower energy state than Mn_2O_3 and the catalyst totally is in the state of lower than +3 in oxidation number. Silver atom can be said to have an oxidation number of +1 because it is in the same energy state as Ag_2O. However, it was also presumed that silver atom formed a double oxide with manganese because the peak intensity of Ag_2O was weak in XRD pattern of Fig. 6. Peaks of Mn_3O_4 and $AgMn_2O_4$

were recognized in XRD pattern of example 4 of Fig. 7 and presence of double oxide which was foreseen in Example 2 was confirmed. According to XRD pattern of Comparative Example 3 shown in Fig. 5, in the composition of high silver content which showed no double oxide effect in the results of Example 1 of Fig. 1, the silver was precipitated in metallic state and it can be said from the results that one of the factors for high activation is that silver is in an oxidation state.

Example 6

29.3 g of silver nitrate and 97.6 g of manganese nitrate hexahydrate were dissolved in distilled water to obtain 400 cc of a mixed aqueous solution. γ-alumina honeycomb having a specific surface area of 150 m^2/g and having 100 cells/$inch^2$ was dipped in the above mixed aqueous solution for 2 minutes, then dried at 120°C and thereafter, heat treated at 500°C for 1 hour in air atmosphere. This procedure was repeated twice to obtain a final catalyst. This catalyst had an atomic ratio Ag:Mn=30:70.

Example 7

A catalyst was prepared in the same manner as in Example 6 except that 8.90 g of silver nitrate and 134.4 g of manganese nitrate hexahydrate were used. This catalyst had an atomic ratio Ag:Mn=10:90.

Example 8

5.31 g of silver nitrate, 80.4 g of manganese nitrage hexahydrate, 100 g of γ-alumina powder of 250 m^2/g in specific surface area, and 40 cc of distilled water were kneaded for about 1 hour. The resulting slurry was dried at 120°C and then, fired at 500°C for 2 hours.

The resulting oxide was classified into 200 mesh or less and a binder and distilled water were added thereto to prepare a slurry. This slurry was coated on a cordierite honeycomb having 100 cells/$inch^2$ and this was dried at 120°C and fired at 500°C for 2 hours.

Comparative Example 4

A silver catalyst was prepared in the same manner as in Example 6 except that 79.41 g of silver nitrate was used and manganese nitrate hexahydrate was not used.

Comparative Example 5

A manganese oxide catalsyt was prepared in the same manner as in Example 7 except that silver nitrate was not used and 183.27 g of manganese nitrate hexahydrate was used.

Comparative Example 6

Aqueous ammonia was added dropwise to a solution prepared by dissolving 48.2 g of silver nitrate in 1 liter of distilled water and the resulting sol was

filtered and dried and then fired at 500°C for 2 hours to obtain silver catalyst powder. Separately, aqueous ammonia was added dropwise to a solution prepared by dissolving 75.6 g of manganese nitrate hexahydrate in 1 liter of distilled water and the resulting sol was filtered and dried and then, fired at 500°C for 2 hours to obtain manganese oxide. The silver catalyst, the manganese oxide and γ-alumina powder having a specific surface area of 250 m^2/g were mixed in a weight ratio of 3:7:90 and wet kneaded. The mixture was dried and press molded and classified to 40-68 meshes to obtain a catalyst. Peaks of γ-alumina, Ag, and MnO_2 were seen in X-ray diffraction pattern of this catalyst.

Removing rate was measured on the catalysts of Examples 6, 7 and 8 and Comparative Examples 4, 5 and 6 at reaction temperatures of 100°C, 200°C and 300°C under the conditions of SV: 30000 h^{-1} and reaction gas: 60 ppm of acetaldehyde, 60 ppm of trimethylamine and air as a base. The results are shown in Fig. 8.

The catalysts of examples 6, 7 and 8 were higher in removing rate than those of Comparative Examples 4, 5 and 6 and especially were high in activity at 100-300°C. Therefore, the catalysts of Examples 6, 7 and 8 show effective catalyst activities even if the temperature of disagreeable odor gas generated is low. In the case of such system as heating the disagreeable odor gas or catalyst by heater to keep a high reaction temperature, the effect can be exhibited without causing

slipping of gas even at a low temperature during elevation of temperature by heater.

Example 9

25.48 g of silver nitrate and 43.06 g of manganese nitrate hexahydrate were dissolved in 2 liters of distilled water to obtain a mixed aqueous solution. Aqueous ammonia prepared by diluting concentrated aqueous ammonia with distilled water twice in volume was added dropwise to the above mixed aqueous solution with stirring to produce a precipitate. This precipitate was washed twice by decantation, then subjected to suction filtration and dried at 120°C. This was fired at 300°C for 2 hours to obtain a catalyst.

The catalyst was analyzed by powder X-ray diffraction. The X-ray diffraction pattern thereof is shown in Fig. 9. In Fig. 9, ∇ shows a peak peculiar to Mn_2O_3 and $\blacktriangledown$ shows a peak peculiar to $AgMn_2O_4$. Therefrom it can be seen that the catalyst contained manganese oxide and double oxide of silver and manganese.

Example 10

A coating slurry was prepared in the same manner as in Example 9 except that 68.66 g of manganese acetate tetrahydrate was used in place of manganese nitrate hexahydrate. This was coated on a metal gauze of stainless steel on which alumina had been flame sprayed and dried and then fired at 500°C for 2 hours. Using a stack of 22

sheets of this metal gauze type catalyst, the removing rate was measured at a reaction temperature of 250°C under the conditions of SV: 30000 h^{-1} and reaction gas: 50 ppm of acetaldehyde, 50 ppm of trimethylamine and air as a base. In this case, the removing rate of acetaldehyde was 80% and that of trimethylamine was 90%. Since this metal gauze type catalyst had a higher thermal conductivity than catalyst comprising only an oxide, the temperature of the catalyst layer rapidly increased by the reaction gas or the heater and this catalyst was also found to be systemically effective.

Example 11

A catalyst was prepared in the same manner as in Example 6 except that 8.90 g of silver nitrate, 134.4 g of manganese nitrate and 13.265 g of cobalt nitrate were used. This catalyst had an atomic ratio Ag:Mn=10:90 and atomic % of Co in total number of such atoms Ag, Mn and Co was 8%.

Comparative Example 7

A catalyst was prepared in the same manner as in Example 6 except that 8.90 g of silver nitrate, 134.4 g of manganese nitrate and 138.472 g of cobalt nitrate were used. This catalyst had an atomic ratio Ag:Mn=10:90 and atomic % of Co in total number of such atoms as Ag, Mn and Co was 50%.

Under the same experimental conditions as in

obtaining the data of Fig. 10, the acetaldehyde removing rate was measured for catalysts of Examples 7 and 11 and Comparative Example 7. The catalyst of Example 11 which corresponds to the catalyst of Example 7 to which 8% by atom of Co was added had substantially no difference in activity from that of Example 7. However, the catalyst of Comparative Exmaple 7 which corresponds to the catalyst of Example 7 to which Co atom was added in an amount of 50% by atom was inferior in activity to the catalyst of Example 7.

Using the catalyst of Example 7, removing rates at reaction temperatures of 100, 200, and 300°C were measured under the conditions of SV=30000 h^{-1} and reaction gas comprising 60 ppm of methyl mercaptan (CH_3SH) and air as a base. The results are shown in Fig. 11. Mercaptan was generated when meats or vegetables decayed. An example of generation of such an odor component is a wet refuse deodorizer. Fig. 14 shows an example of a wet refuse deodorizer provided with the catalyst of the present invention. An exhaust vent for discharging gas generated from the wet refuse is provided at cover 301 of deodorizer 300 and in this exhaust vent are provided catalsyt 302, a heater 304 for heating catalyst layer 302 and a fan 303 for discharging the gas deodorized by the catalyst layer 302. The results of measurement of removing rate of mercaptan for application of the catalyst to such use was that the removing

rate was 80% at a reaction temperature of 100°C and the catalyst showed a high activity at the low temperature.

CLAIMS:-

1. A catalyst for oxidation or decomposition of a gas containing odor components in the presence of oxygen, thereby making the gas harmless, which comprises a carrier and an active component supported on the carrier and which contains, as the active component, silver and manganese in an atomic ratio of silver to manganese of 5:95 to 50:50 and contains silver as at least one component selected from the group consisting of a compound with oxygen and a compound with oxygen and manganese and manganese as at least one component selected from the group consisting of a compound with oxygen and a compound with oxygen and silver, at least the manganese oxide containing a manganese atom having an oxidation number of less than +4.

2. A catalyst according to claim 1, wherein the carrier has a specific surface area of 0.5 to 1000 m^2/g.

3. A catalyst according to claim 1, wherein the carrier is one member selected from the group consisting of γ-alumina, TiO_2, zeolite, silica and cordierite.

4. A catalyst according to claim 1, which contains at least one manganese oxide selected from the group consisting of Mn_2O_3 and Mn_3O_4.

5. A catalyst for oxidation or decomposition of a gas containing odor components in the presence of oxygen, thereby making the gas harmless, which comprises a carrier and an active component supported on the carrier, which is coated on a honeycomb-like, plate-like

or metal gauze-like substrate comprising ceramics or metal, and which contains, as the active component, silver and manganese in an atomic ratio of silver to manganese of 5:95 to 50:50 and contains silver as at least one component selected from the group consisting of a compound with oxygen and a compound with oxygen and manganese and manganese as at least one component selected from the group consisting of a compound with oxygen and a compound with oxygen and silver, at least the manganese oxide containing a manganese atom having an oxidation number of less than +4.

6. A catalyst for oxidation or decomposition of a gas containing odor components in the presence of oxygen, thereby making the gas harmless, which comprises a carrier and an active component supported on the carrier and which contains, as the active component, silver and manganese in an atomic ratio of silver to manganese of 5:95 to 50:50 and contains silver as at least one component selected from the group consisting of a compound with oxygen and a compound with oxygen and manganese and manganese as at least one component selected from the group consisting of a compound with oxygen and a compound with oxygen and silver, at least the manganese oxide containing a manganese atom having a oxidation number of less than +4, the active component being prepared by mixing at least one compound selected from the group consisting of a silver salt and silver oxide with at least one compound selected from

the group consisting of a manganese salt and manganese oxide and finally heat treating the mixture at 200 to 900°C in the presence of an oxygen-containing gas.

7. A catalyst for oxidation or decomposition of a gas containing odor components in the presence of oxygen, thereby making the gas harmless, which comprises a carrier and an active component supported on the carrier, which is coated on a honeycomb-like, plate-like or metal gauze-like substrate comprising ceramics or metal, and which contains, as the active component, silver and manganese in an atomic ratio of silver to manganese of 5:95 to 50;50 and contains silver as at least one component selected from the group consisting of a compound with oxygen and a compound with oxygen and manganese and manganese as at least one component selected from the group consisting of a compound with oxygen and a compound with oxygen and silver, at least the manganese oxide containing a manganese atom having an oxidation number of less than +4, the active component being prepared by mixing at least one compound selected from the group consisting of a silver salt and silver oxide with at elast one compound selected from the group consisting of a manganese salt and manganese oxide and finally heat treating the mixture at 200 to 900°C in the presence of air.

8. A catalyst for oxidation or decomposition of a gas containing odor components in the presence of oxygen, thereby making the gas harmless, which comprises

a carrier and an active component supported on the carrier and which contains, as the active component, silver and manganese in an atomic ratio of silver to manganese of 5:95 to 50:50 and 1 to 10% by atom, based on the active component, of at least one element selected from the group consisting of iron, cobalt, nickel, copper, vanadium, zinc and noble metals of Group VIII of the periodic table and contains silver as at least one component selected from the group consisting of a compound with oxygen and a compound with oxygen and manganese, manganese as at least one component selected from the group consisting of a compound with oxygen and a compound with oxygen and silver and iron, cobalt, nickel, copper, vanadium, and zinc as an oxide and contains the noble metal as element or an oxide, at least the manganese oxide containing a manganese atom having an oxidation number of less than +4.

9. A catalyst for oxidation or decomposition of a gas containing odor components in the presence of oxygen, thereby making the gas harmless, which comprises a carrier and an active component supported on the carrier, which is coated on a honeycomb-like, plate-like or metal gauze-like substrate, and which contains, as the active component, silver and manganese in an atomic ratio of silver to manganese of 5:95 to 50:50 and 1 to 10% by atom, based on the active component, of at least one element selected from the group consisting of iron, cobalt,

nickel, copper, vanadium, zinc and noble metals of Group VIII of the periodic table and contains silver as at least one component selected from the group consisting of a compound with oxygen and a compound with oxygen and manganese, manganese as at least one component selected from the group consisting of a compound with oxygen and a compound with oxygen and silver and contains iron, cobalt, nickel, copper, vanadium, and zinc as an oxide and the noble metal of Group VIII of the periodic table as element or an oxide, at least the manganese oxide containing a manganese atom having an oxidation number of less than +4.

10. A catalyst for oxidation or decomposition of a gas containing odor components in the presence of oxygen, thereby making the gas harmless, which contains, as an active component, silver and manganese in an atomic ratio of silver to manganese of 5:95 to 50:50 and contains silver as at least one component selected from the group consisting of a compound with oxygen and a compound with oxygen and manganese and manganese as at least one component selected from the group consisting of a compound with oxygen and a compound with oxygen and silver, at least the manganese oxide containing a manganese atom having an oxidation number of less than +4.

11. A catalyst for oxidation or decomposition of a gas containing odor components in the presence of oxygen, thereby making the gas harmless, which contains,

as an active component, silver and manganese in an atomic ratio of silver to manganese of 5:95 to 50:50 and 1 to 10% by atom, based on the active component, of at least one element selected from the group consisting of iron, cobalt, nickel, copper, vanadium, zinc and noble metals of group VIII of the periodic table and contains silver as at least one component selected from the group consisting of a compound with oxygen and a compound with oxygen and manganese, manganese as at least one component selected from the group consisting of a compound with oxygen and a compound with oxygen and silver and contains iron, cobalt, nickel, copper, vanadium, and zinc as an oxide and the noble metal of Group VIII of the periodic table as element or an oxide, at least the manganese oxide containing a manganese atom having an oxidation number of less than +4.

12. A catalyst for oxidation or decomposition of a gas containing odor components at a temperature of from room temeprature to 300°C in the presence of oxygen, thereby making the gas harmless, which comprises a carrier and an active component supported on the carrier and which contains, as the active component, silver and manganese in an atomic ratio of silver to manganese of 5:95 to 50:50 and contains silver as at least one component selected from the group consisting of a compound with oxygen and a compound with oxygen and manganese and manganese as at least one component selected from the group consisting of a compound with oxygen and a

compound with oxygen and silver, at least the manganese oxide containing a manganese atom having an oxidation number of less than +4.

13. A cooking utensil, which comprises a grill for cooking a food by heating, a heater for the grill and an exhaust vent for discharging a gas containing odor components generated in the grill, the exhaust vent being provided with a catalyst layer which comprises a carrier and an active component supported on the carirer and which contains, as the active component, silver and manganese is an atomic ratio of silver to manganese of 5:95 to 50:50 and contains silver as at least one component selected from the group consisting of a compound with oxygen and a compound with oxygen and manganese and manganese as at least one component selected from the group consisting of a compound with oxygen and a compound with oxygen and silver, at least the manganese oxide containing a manganese atom having an oxidation number of less than +4.

14. A cooking utensil according to claim 13, which is an oven, a gas oven, an electronic oven or a gas table.

15. An industrial waste disposal equipment, which comprises an incinerator for incinerating industrial wastes and an exhausting means for an off-gas containing odor components generated in the incinerator, the exhausting means being provided with a catalyst layer which comprises a carrier and an active component supported

on the carrier and which contains, as the active component, silver and manganese in an atomic ratio of silver to manganese of 5:95 to 50:50 and contains silver as at least one component selected from the group consisting of a compound with oxygen and a compound with oxygen and manganese and manganese as at least one component selected from the group consisting of a compound with oxygen and a compound with oxygen and silver, at least the manganese oxide containing a manganese atom having an oxidation number of less than +4.

16. A wet refuse deodorizer, which comprises a container for containing wet refuses provided with an exhaust vent for gas generated in the container, the exhaust vent being provided with a catalyst layer which comprises a carrier and an active component supported on the carrier and which contains, as the active component, silver and manganese in an atomic ratio of silver to manganese of 5:95 to 50:50 and contains silver as at least one component selected from the group consisting of a compound with oxygen and a compound with oxygen and manganese and manganese as at least one component selected from the group consisting of a compound with oxygen and a compound with oxygen and silver, at least the manganese oxide containing a manganese atom having an oxidation number of less than +4.

17. A vehicle for carrying men or cargoes, which comprises a catalyst layer provided near a position where men or cargoes are present, the catalyst layer which comprises

a carrier and an active component supported on the carrier and which contains, as the active component, silver and manganese in an atomic ratio of silver to manganese of 5:95 to 50:50 and contains silver as at least one component selected from the group consisting of a compound with oxygen and a compound with oxygen and manganese and manganese as at least one component selected from the group consisting of a compound with oxygen and a compound with oxygen and silver, at least the manganese oxide containing a manganese atom having an oxidation number of less than +4, and an exhausting means for discharging gas deodorized by the catalyst layer.

18. A toilet, which comprises a toilet stool and an exhaust vent for discharging gas containing odor components generated by use of the toilet stool, the exhaust vent being provided with a catalyst layer which comprises a carrier and an active component supported on the carrier and which contains, as the active component, silver and manganese in an atomic ratio of silver to manganese of 5:95 to 50:50 and contains silver as at least one component selected from the group consisting of a compound with oxygen and a compound with oxygen and manganese and manganese as at least one component selected from the group consisting of a compound with oxygen and a compound with oxygen and silver, at least the manganese oxide containing a manganese atom having an oxidation number of less than +4 and a heater for

heating the catalyst layer to a temperature of from room temperature to 300°C provided at a position before the catalyst layer in the exhaust vent.

19. A cartridge type deodorizing catalyst which comprises a carrier and an active component supported on the carrier which are provided on a substrate and which contains, as the active component, silver and manganese in an atomic ratio of silver to manganese of 5:95 to 50:50 and contains silver as at least one component selected from the group consisting of a compound with oxygen and a compound with oxygen and manganese and manganese as at least one component selected from the group consisting of a compound with oxygen and a compound with oxygen and silver, at least the manganese oxide containing a manganese atom having an oxidation number of less than +4.

20. A method for use of a catalyst which comprises contacting a gas containing odor components with a catalyst which comprises a carrier and an active component supported on the carrier and which contains, as the active component, silver and manganese in an atomic ratio of silver to manganese of 5:95 to 50:50 and contains silver as at least one component selected from the group consisting of a compound with oxygen and a compound with oxygen and manganese and manganese as at least one component selected from the group consisting of a compound with oxygen and a compound with oxygen and silver, at least the manganese oxide containing a

manganese atom having an oxidation number of less than +4 in the presence of oxygen at a temperature of from room temperature to 300°C, thereby oxidizing or decomposing the gas containing odor components.

21. A catalyst for oxidation or decomposition of a gas containing odor components in the presence of oxygen substantially as herein described with reference to the accompanying drawings.

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